

SPECIFICATION

INVENTOR: VENKAT K RAGHAVENDRAN

TITLE: IMPROVED GLASS MAT THERMOPLASTIC COMPOSITE

FIELD OF THE INVENTION

The present invention relates to a glass mat thermoplastic (GMT) composite, and more particularly to glass mat thermoplastic (GMT) composite having a Class-A surface made with a blend of thermoplastic resins and polymerizable moieties providing a resin rich surface finish when heated and molded using thermoforming and compression molding tools.

BACKGROUND OF THE INVENTION

There is a growing demand by industry, governmental regulatory agencies and consumers for durable and inexpensive products that are functional comparable or superior to metal products. This is particularly true in the automotive industry. Developers and manufacturers of these products are concerned with the strength parameters, such as impact, bending, stretching, and twisting resilience. To meet these demands, a number of composite materials have been engineered. A relatively inexpensive product is GMT composite. GMT composites can be molded and stamped into a variety of suitable products, most notably are bumpers. Previous known GMT products do not have sufficiently good surface qualities to be used in visible applications on automobiles, such as body panels. The quality of the finish has to be suitable for painting, and

this surface finish is designated a Class-A surface. Currently only sheet molded compounds (SMC) are used on visible, painted automobile body components. SMCs are substantially more expensive than GMT fabricated parts, and generate a lot of scrap. What is needed is a GMT that has a Class-A surface that can be used in visible, painted parts. A review of the prior art follows:

DESCRIPTION OF THE PRIOR ART

Applicant is aware of the following U. S. Patents.

<u>US Pat. No.</u>	<u>Inventor</u>	<u>Issue Date</u>	<u>Title</u>
4,983,247	Kim	Jan. 8, 1991	METHOD FOR PRODUCING RESIN RICH SURFACE LAYER ON COMPOSITE THERMOPLASTIC MATERIAL
5,464,585	Fitzgibbon	Nov. 7, 1995	METHOD OF INJECTION MOLDING ARTICLES WITH SELECTIVE CONCENTRATIONS OR GRADIENTS OF MATERIALS
4,612,238	Della Vecchia	Sept 16, 1986	FIBER REINFORCED MULTI-PLY STAMPABLE THERMOPLASTIC SHEET

Kim, in U.S. Patent 4,983,247, teaches a method for making a fiber reinforced composite having a resin rich first layer on the surface. Forming a fiber free layer of a thermoplastic resin, heating a composite bulk layer of resin and reinforcing fibers, and then compressing the first layer and the composite bulk layer, so that the heat from the bulk layer causes the first layer to melt.

Fitzgibbon, in U. S. Patent 5,464,585, teaches a method where a resin-modifying auxiliary material is concentrated in the surface portion of an article. The method is particularly suited to RIM (reaction injection molding). In the process the mold is filled with a gradient of a bulk material and an auxiliary material, where the auxiliary material is generally defined as producing superior results as a mold surface material. The ratio is varied with time, so that as the mold is filled there is less of the auxiliary material. Cited along with resin-modifying auxiliary materials are a catalyst and catalyst/initiator for polymerization, wherein they are concentrated at the surface of the mold.

Della Vecchia et al, in US Patent 4,612,238, discloses a process for producing a laminate that combines a layer of resin, a glass mat, another layer of resin, a second glass mat, and a third layer of resin. The first and third layers of resin, which are thermoplastic materials, can be selected so as to obtain the desired properties. Various quantities of reinforcing materials, fillers and additives can be in selected proportions.

SUMMARY OF THE INVENTION

The invention is a method for manufacturing and composition of a fiber reinforced laminate material of a multi-layered laminate having two or more layers, wherein following heating and compression molding or thermoforming the laminate material forms a composite having a Class-A surface that is resin rich. The fiber reinforced laminate material is typically utilized to make GMT composites that have a Class-A surface. The fiber reinforced laminate material is a multi-layered laminate that is formed with two or more layers, comprising: a layer comprised of a thermoplastic resin; a layer comprised of a polymerizable component comprised of chemically reactive components; and /or a layer of reinforcing fibers. The layers can be combined such that there is at least one layer of reinforcing fibers and a layer of a thermoplastic resin (A laminate), or at least one layer of reinforcing fibers and a layer of a polymerizable

component (B laminate). The A laminate can in a subsequent coating, or simultaneously, be extrusion coated with a layer of the polymerizable component forming a three layer laminate (C laminate). Alternatively, the B laminate can in a subsequent coating, or simultaneously, be extrusion coated with a layer of the thermoplastic resin, which therein forms a three layer laminate that is also the C laminate. It obviously follows that the multi-layered laminates can be other combinations of the at least two layer laminate. For instance, CBBC and CCC, or two A laminates could be combined with an extrusion coating of the polymerizable component layer, wherein the thermoplastic resin layers are outer layers. This last combination is the conventional five layer GMT composite. Typically, the thermoplastic resin layer is further comprised of a polymerization agent selected from the group consisting of initiators, accelerators, cross-linkers, catalysts, drying agents, and a combination thereof. The polymerization agent need not be equally distributed throughout the thermoplastic resin, but can be added as a coating to the layer of thermoplastic resin. The polymerizable component layer and the thermoplastic resin layer are preferably separated by the layer of reinforcing fibers. The polymerizable component contains chemically reactive compounds selected from the group consisting of low molecular weight polymers, macrocyclic oligomers, oligomers, prepolymers, monomers, dimers, trimers, tetramers and the like, or any combination thereof. The polymerizable component can be further comprised of a thermoplastic polymer, such as the thermoplastic resin. The reinforced fiber layer is comprised of fibers selected from the group consisting of glass fibers, metal fibers, ceramic fibers, carbon fibers, aramid fibers, synthetic polymers made from polymers such as polyester, polypropylene, polyamides, polyimides, and polyurethanes, and blends of combinations thereof. The fibers can be chopped, matted, picked, bonded, woven, and other wise processed to optimize handling, saturation, cost, strength and orientation. In a preferred embodiment the thermoplastic layer is extruded onto a first side of the layer of reinforcing fibers, and the polymerizable component layer is extruded onto the opposing side of the reinforcing fiber layer. The chemically reactive compounds and the polymerization agents are selected so that when heated, the chemically reactive compounds polymerize forming a Class-A surface finish. The reinforcing fiber layer is selected so as to impart strength to the laminate following B-stage

processing. In B-stage processing, at least one A laminate is combined with the polymerizable component or the C laminate in a thermoforming or compression molding process, wherein the laminates are heated and molded under compression. Preferably the laminates are combined such that the polymerizable component is sandwiched by the reinforcing fiber layers.

The reinforcing fiber layer is further selected to be sufficiently open as to be permeable to impregnation / saturation by the thermoplastic resin, and to enable the permeation of the chemically reactive components, when the laminate is under heat and compression. Prior to reaction, the polymerizable layer has a lower viscosity when heated than the thermoplastic layer at the elevated temperatures. The compression and heat cause the lower viscosity polymerizable layer to flow faster than the thermoplastic resin layer.

To produce the GMT composite having a Class-A surface, the multilayered laminate is preferably prepared as a five layer laminate comprised of a pair of outer layers of thermoplastic resin that sandwich two reinforcing fiber layers, which have a core of the polymerizable component layer. In B-stage processing, under heat and pressure the polymerizable component layer permeates the reinforcing fiber layers, thereby coming into contact with the thermoplastic resin layer. The reactive compounds initially act as a flux and facilitate the penetration of thermoplastic resin into the reinforced fiber layers. Similarly, the chemically reactive compounds come into the sphere of influence of the polymerization agent, which initiates / catalyzes the polymerization of the chemically reactive compounds. A portion of the chemically reactive compounds are carried to the surface of the multilayered laminate, wherein they continue to polymerize forming a Class-A surface, that is substantially fiber free. The thermoplastic resin thoroughly permeates the reinforcing fiber forming a composite having a core with a nearly uniform mixture of reinforced fiber and interstitial polymer, and a surface layer comprised of the now polymerized chemically reactive compounds. The finish of the surface coating substantially replicates the mold or compression plate.

The thermoplastic layer can be compounded to include other additives such as reinforcing fibers, extenders which are fillers, antioxidants, UV stabilizers, thermal stabilizers, flame retardants, fillers which are reinforcing, glass beads, colorants, antimicrobial agents, dyes, pigments, plasticizers, oils, impact modifiers, processing aides (i.e. waxes, fluorinated compounds, silicone compounds, surfactants, polymeric processing aides), density modifiers such as phenolic beads, desiccants, buffers, and IR absorbent compounds to facilitate heating (i.e. carbon blacks, graphite, metal oxides). Similarly the polymerizable component layer and the reinforced fiber layer can contain similar additives.

In this respect, before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to the detailed construction and to the arrangements of the components set forth in the following description illustrated in the drawings. The invention is capable of other embodiments and of being practiced and carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein are for the purpose of the description and should not be regarded as limiting.

OBJECTS OF THE INVENTION

The principal object of the present invention is to provide an improved composition for forming a fiber reinforced thermoplastic composite, that following compression and heating, said composite has a Class-A surface.

A further object of this invention is to provide an improved composition for forming a fiber reinforced composite, wherein the surface of the composite has a polymerized coating with attendant resistance to chemical etching.

A further object of this invention is to provide a composition for a fiber reinforced laminate material, wherein the core of the composite is comprised of polymer that is integrally admixed with the reinforcing fibers.

Another object of the invention is to provide an improved composition for a GMT composite, wherein parts fabricated from a GMT composite can either be in-mold coated or painted in subsequent steps for use in exterior body panel applications in automotive and transportation markets.

BRIEF DESCRIPTION OF THE DRAWINGS

The foregoing and other objects will become more readily apparent by referring to the following detailed description and the appended drawings in which:

Figure 1 depicts the layered structure of the laminate sheet being consolidated using a double belt laminator.

Figure 2. shows the formation of the resin rich surface of the composite formed in the tool.

DETAILED DESCRIPTION

The invention is a GMT laminate material that following thermoforming or compression molding forms a GMT laminate part with a Class-A surface, wherein the GMT part is suitable for

applications as an exterior body panel. The body part can be either in-mold coated, or painted in subsequent steps for use in exterior body panel applications in the automotive and transportation markets. The GMT laminate material **10** is typically a five-layered structure consisting of two layers of reinforcing fibrous mat sandwiching a polymerizable component core layer and an overlayer of thermoplastic resin on either side of the reinforcing fibrous mat. The polymerizable component layer **14** and the two thermoplastic resin layers, **12** and **22**, are extruded on the layers of glass fibrous mat, **16** and **18**, as shown in Figure 1. This five-layered structure is passed through a double belt laminator consisting of heated belts, **42** and **40**, to melt and impregnate the resin through the glass fibrous mat, therein consolidating the structure. A pair of cooling belts, **52** and **50**, removes the heat and solidifies the resins to form a laminate **10** of the GMT material. As shown in Figure 2, under heat and pressure the GMT laminate material **10** fuses forming a composite with a Class A surface **100**. The core **102** is comprised of the glass fibers integrally mixed with the thermoplastic resin. The surface of the composite **100** has a resin rich surface **104** substantially comprised of the chemically reactive component that is now polymerized. Note, under heat and pressure, the chemically reactive component has migrated from the core to the surface of the composite.

A preferred thermoplastic resin comprising the thermoplastic resin layer is a polycarbonate resin that has melt flow index (MFI) greater than 5 and less than 28, with a preferred MFI greater than 12. The preferred polycarbonate is based on bisphenol-A. The polycarbonate resin is compounded with a filler, calcium carbonate, a reinforcing chopped fiber, and a polymerization agent. The preferred polymerization agent can be a free radical, anionic or transesterification catalyst. In the instant case, the polymerizable component is to be polymerized via transesterification. Suitable transesterification catalyst for polymerizing macrocyclic oligoesters, are selected from the group consisting of organotin and organotitanate compounds. Examples of organotin compounds are dibutyltin dioxide, 1,1,6,6-tetra-n-butyl-1,6-distanna-2,5,7,10-tetraoxacyclodecane, n-butyltin(IV) chloride dihydroxide, dialkyltin(IV) oxides, such as di-n-butyltin(IV) oxide and di-n-octyltin oxide, and acyclic and cyclic monoalkyltin(IV)

derivatives such as n-butyltin tri-n-butoxide, dialkyltin(IV) dialkoxides such as di-n-butyltin(IV) di-n-butoxide and 2,2-di-n-butyl-2-stanna-1,3-dioxacycloheptane, and trialkyltin alkoxides such as tributyltin ethoxide. Examples of organotitanate compounds are tetra-isopropyl titanate tetra(2-ethylhexyl) titanate, tetraisopropyl titanate, and tetrabutyl titanate, and isopropyl triethanolaminatitanate. These catalyst can also be employed when the polymerizable composition includes a monomer, such as a cyclic ester (i.e. ϵ -caprolactone), which can be added to reduce the melting point of the macrocyclic polyester oligomers. The polymerizable component layer is preferably comprised of a macrocyclic oligoester). The polymerizable component layer is comprised of reactive compounds, preferably a macrocyclic polyester oligomers, also known as a macrocyclic oligoester. The macrocyclic oligoester contains 2 or more identifiable ester functional repeat units of the same or different formula. The macrocyclic oligoester typically refers to multiple molecules of one specific formula having varying ring sizes. However, a macrocyclic oligoester may also include multiple molecules of different formulae having varying numbers of the same or different structural repeat units. A macrocyclic oligoester may be a co-oligoester or multi-oligoester, i.e., an oligoester having two or more different structural repeat units having an ester functionality within one cyclic molecule. The macrocyclic oligoester preferably has 3 – 20 structural repeat units. Macrocyclic polyesters have very low viscosities compared to similar weight linear oligomers. In the presence of a polymerization agent, macrocyclic oligoesters can be rapidly polymerized, by ring opening, forming substantially linear polyesters having a much higher molecular weight. Typical molecular weights are in the range from about 90,000 to in excess of 150,000. The reaction has a relatively low exotherm. Preferred macrocyclic oligoesters are macrocyclic oligoesters of 1,4-butylene terephthalate (CBT), 1,3-propylene terephthalate (CPT), 1,4-cyclohexylenedimethylene terephthalate (CCT), ethylene terephthalate (CET), and 1,2-ethylene 2,6-naphthalenedicarboxylate (CEN). Macrocyclic multi-oligoesters are comprised of two or more of the above structural repeat units. The scope of the invention includes macrocyclic oligoesters of polyethylene isophthalate, sulfonated polyethylene isophthalate, sulfonated polyalkylene terephthalate, sulfonated polyalkylene naphthenate, and sulfonated polyalkylene isophthalate. As previously mentioned

monomers can be added, serving principally as diluents and also cross-linkers. Macrocyclic oligoesters can be blended to change the miscibility of the macrocyclic oligoester in the thermoplastic resin, and to change the melting point. Also, linear oligomers can be admixed with macrocyclic oligoesters to lower the melting point. The mixing of isophthalate esters to terephthalate esters significantly reduces the crystallinity of the polymerized material. The main advantage of macrocyclic oligoesters over their linear counterpart is that upon melting they have a very low viscosity. For instance, CBT resins are solid (powder, pellet, flake) at room temperature and when heated are fully molten above 150°C (300°F), with a viscosity in the range of 150 mPa.s (150 cP), and drops in viscosity to below 20 mPa.s (20 cP) at 180°C (355 °F). When mixed with specific tin or titanium polymerization catalysts the PBT macrocyclic oligoesters open and connect (i.e., polymerize) to form high molecular weight PBT thermoplastic without exotherm or off-gassing. Full polymerization can occur in 10's of seconds or many minutes depending on the temperature and type of catalyst used. The initial water-like viscosity enables the resin to migrate to the surface during B-stage processing. As a comparison of viscosity, polycarbonate having a MFI of 18 – 24 has a viscosity 40,000 mPa (40,000 cP) at 600 °F, while CBT has a viscosity of 5 mPa (5 cP). Typically, the polymerizable component layer has a significant percentage of polycarbonate to improve the filmic properties, wherein the polycarbonate can make up to 80% of the extruded polymerizable component layer.

An example of the invention is given in Example 1.

EXAMPLE 1

A 2.1 oz/sq. ft glass fiber mat is extrusion coated with a filled polycarbonate resin. The polycarbonate resin is a GE Lexan® HF1110 polycarbonate resin having a Melt Flow Index (MFI) listed as 18-24 g/10 min (a.k.a. Melt Flow Rate (MFR) = 18-24 g/10 min). The polycarbonate resin is admixed with polymerization agent that is a titanate ester, isopropyl triethanolaminatitanate. Isopropyl triethanolaminatitanate is sold by E.I. Dupont de Nemours

under trade name Tyzor AA105, and is a catalyst for the transesterification polymerization of macrocyclic oligoesters. The isopropyl triethanolaminatitanate is compounded with the polycarbonate resin at 0.5 mol %. The thermoplastic resin is extruded at about 2 oz/sq. ft. A second glass fiber mat weighing 2.1 oz/sq. ft containing is similarly coated. Coextruded between the two mats is a polymerizable component layer comprised of about 75% by weight GE Lexan HF1110 polycarbonate and 25% by weight cyclic butylene tererphthalate macrocyclic oligoester (CBT) mixture. The polymerizable component layer extrudate weighs about 8 oz/sq.ft. The total weight of the five layer GMT structure is about 16 oz/ sq. ft.

The five layer structure is pressed in a heated press with platen surface temperature measuring 600 °F for about 4 minutes. The platens are held at a constant gap of 3 mm. The heated product is transported to a cooling press and cooled to room temperature under pressure at a constant gap of 3 mm for about 4 minutes, forming a GMT laminate material. The cooled laminate sheet is then trimmed, sheared and sectioned into 8" square panels.

In B-stage processing, the laminate material is heated in an IR oven to 600 °F for 120 seconds and thermoformed or compression molded in a heated tool held at 200 °F with a pressure of 2 tons/sq in. The resulting composite has a uniform core of polycarbonate and GMT and a Class A surface with a tool surface finish. The composite has an impact strength and tensile as shown below.

GLASS CONTENT	%	29
IMPACT STRENGTH	ft-lb./in.	20
TENSILE STRENGTH	ksi	19.2
TENSILE MODULUS	ksi	1045
MULTIAXIAL IMPACT	ft-lbs	13.5 Max Load
	ft-lbs	20.3 Failure

**SUMMARY OF THE ACHIEVEMENT
OF THE OBJECTS OF THE INVENTION**

From the foregoing, it is readily apparent that I have invented an improved composition for forming a fiber reinforced composite, wherein the surface of the composite has a resin coating that is substantially free of glass fibers. It is also apparent that I have provided a composition for a fiber reinforced laminate material, wherein, after thermoforming or molding, the core of the composite is substantially comprised of thermoplastic resin polymer that is integrally admixed with the reinforcing fibers. It is further apparent that the GMT laminate material, when processed by thermoforming or compression molding the resulting manufactured parts are suitable for use in exterior body panel applications in automotive and transportation markets.

It is to be understood that the foregoing description and specific embodiments are merely illustrative of the best mode of the invention and the principles thereof, and that various modifications and additions may be made to the apparatus by those skilled in the art, without departing from the spirit and scope of this invention, which is therefore understood to be limited only by the scope of the appended claims.